

HEXACHLOROXANTHENE ANALYSIS WITH TCDD

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Introduction

The compound 1,2,4,5,7,8-hexachloro-9H-xanthene, or simply termed Hexachloroxanthene (HCX), has proven to be environmentally stable after being introduced into soil. The production of hexachlorophene, which was used in antibacterial soaps and cosmetics in the United States, yields HCX as a by-product¹. Another undesired by-product of the hexachlorophene process is the environmentally stable 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). HCX and TCDD were reported in soil samples over 20 years ago from a variety of sites in Eastern Missouri by Viswanathan and Kleopfer². Several other compounds, produced or used as starting materials for the hexachlorophene process, including 2,4,5-Trichlorophenol (TCP) and 2,4,5-Trichloroanisole (TCA), were found in the contaminated soil. The Eastern Missouri sites also had a conglomerate of uniquely chlorinated compounds that were similarly identified in the original waste oil.

The results shown herein are from two Eastern Missouri sites and an additional site, which is unrelated to the Eastern Missouri contamination. Both qualitative and quantitative determination of the HCX and TCDD are discussed, along with their analytically determined concentrations and ratios.

Methods and Materials**Sample Preparation:**

The samples were extracted using a 16-hour soxhlet extraction, following EPA Method 1613³. Many of the samples required extensive clean-up using silica gel and acid alumina columns. The procedures can be found in EPA Method 1613.

Analysis of Extracts:

The extracts were analyzed for the 2,3,7,8-chlorine containing dioxins and furans at trace levels by GC/HRMS using a VG-ZAB with a 60 m DB-5 column. EPA Method 1613 was used for these analyses. Qualitative and quantitative results for HCX were also reported via GC/HRMS analyses using selected ion monitoring (SIM).

Qualitative Determination of HCX:

The initial determination of the presence of HCX was made by GC/HRMS, collecting full scan data from m/z 100-500. An accurate mass measurement was then obtained of the molecular ion cluster for both one sample and a prepared standard of the HCX. After HCX was proven to be present in a two of the samples by full scan spectral elucidation, the remaining samples were identified by monitoring the selected ions already being used for EPA Method 1613. No modifications were made to Method 1613 to determine either the presence of HCX or the quantitative value in the sample. Two of the selected ion responses used to monitor the hexachlorinated dioxins and furans were used for the qualitative determination of HCX. The first ion monitored was $(M+4)$ m/z 389.8 and the second ion was $(M+6)$ m/z 391.8. Based upon 6 chlorine atoms, the theoretical ion ratio for the monitored ions is 2.31. The PCDD/PCDF

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acceptable ratio for EPA Method 1613 falls within (+/-) 15%, which is equivalent to 2.66 to 1.96 for HCX.

Quantitation of HCX:

The Eastern Missouri work required estimates of HCX concentrations with further qualitative analyses of additional chlorinated compounds. Three standard concentrations of HCX were prepared and analyzed using crystals that were synthesized specifically for this project by Dr. Harry Ensley at Tulane University. HCX concentrations were then determined by comparing sample responses with those of the standards and interpolating the areas of the respective ions.

The analytical requirements at the additional site were somewhat different. A more accurate quantitative determination of HCX was needed, along with low level analyses for the remaining 2,3,7,8-chlorine containing dioxins and furans. Therefore, a five point calibration curve was produced for HCX, from 1 ng to 100 ng injected, based upon a 1 ul injection. The 1,2,3,7,8,9-HxCDF labeled material was used to calculate a response factor. A 10- g extract diluted to a final volume of 20 ul would be calculated as $C = (1 \text{ ng/ul} * 20 \text{ ul}) / 0.01 \text{ kg}$, resulting in a calibration range of 2 ug/kg to 200 ug/kg for HCX.

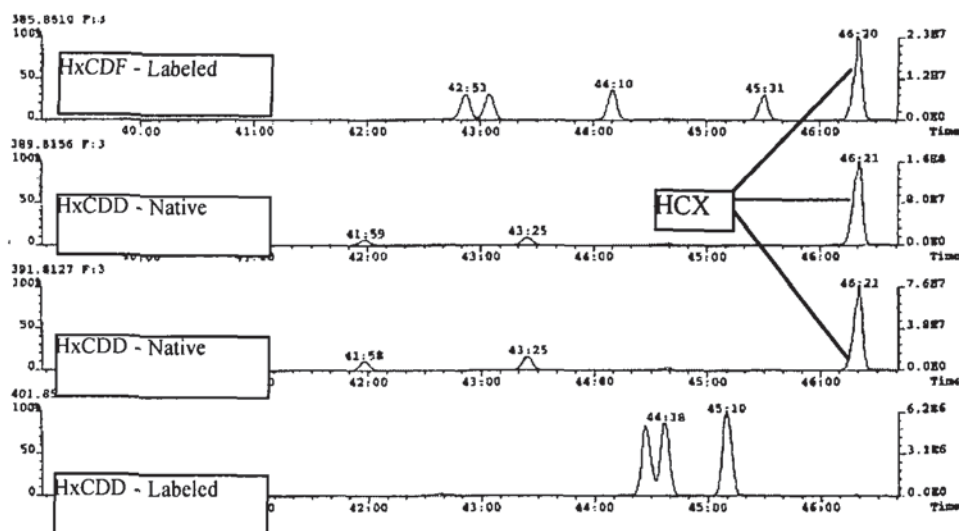


Figure 1 shows four SIM profiles obtained during an analysis using EPA Method 1613. These are also used for the qualitative and quantitative analyses of HCX. The first chromatogram represents the second monitored ion (M+2) of the HxCDF labeled material, which is nearly equivalent to the molecular ion of HCX. The peak at 45:31 represents 1,2,3,7,8,9-HxCDF, used as the internal standard to calculate a response factor. The second and third chromatograms are collected to monitor the response produced from the native HxCDD analytes, (M+2) and (M+4). These also are near the (M+4) and (M+6) ions of HCX, which were used to qualitatively and quantitatively identify HCX. The fourth chromatogram shows three peaks that represent the retention times of the monitored HxCDD labeled analytes.

Results and Discussion

The ratio of HCX concentration to TCDD concentration varied greatly in the early Eastern Missouri sites described by Viswanathan and Kleopfer². The concentration ratio of one site, Denney Farm, had a mean of 2.16 with a %RSD of 27% for 27 samples. The additional 12 sites in that publication significantly deviated from the mean of 2.16, ranging from 0.083 to 66.6. Many possible reasons have been discussed for these ratio differences, including varied reaction conditions, mixing and diluting during application, variance in spraying, possible waste stream differences and differences in volatilities and mobilities of HCX and TCDD^{4,5,6}.

Two additional sites, discovered and characterized in the mid to late 1990's had similar results, shown in the Table, to Denney Farm. Six samples were characterized at the first site, EM-1, and five samples at the second site, EM-2. Many samples were analyzed for TCDD, but only the samples with highest TCDD concentrations were submitted for further characterization. The HCX and TCDD concentrations and ratios appear to be similar to results of 20 years prior. During this characterization, TCA and TCP were also identified, which seems uncharacteristic due to their low vapor pressures.

Additional HCX and TCDD concentrations were obtained from a site unrelated to Eastern Missouri, labeled NR-1. Background surface sediment as well as contaminated surface sediment, at NR-1, were collected for a total of seventy samples. Thirty-one of the 70 extracts had 2,3,7,8-TCDD results below the minimum reporting level of 1ng/kg. Thirty-nine of the extracts had HCX values reported as below the detection limit or did not meet qualitative criteria. The samples which had HCX present and quantified, along with elevated 2,3,7,8-TCDD levels present, are reported in the following Table. The HCX:TCDD ratios ranged from 10.5 – 412, with 25 samples between 10.5 and 35.5. The remaining 5 samples had ratios of 81.4, 56.3, 94.4, 252, 412. These outliers may be due to several possibilities, including the lack of sample homogeneity and inconsistent transport through the river sediment.

Location	No. of Samples	HCX Range	TCDD Range	HCX: TCDD Ratio Range	HCX:TCDD Average Ratio	%RSD
EM-1	6	474-1080	270-1170	0.837-2.67	1.55	46
EM-2	5	114-461	204-461	0.551-2.26	1.15	60
NR-1	30	2.20-209	0.0759-7.47	10.5-412	25.1	250
NR-1	25	2.20-209	0.0759-7.74	10.5-35.5	21.4	31

Lower ratios, but higher concentrations were observed for sites EM-1 and EM-2 compared with site NR-1. Since NR-1 sediments were surface samples, the lower concentrations may be due to vaporization and or photodegradation⁵. Other possibilities include the general mobility of the compounds and possible manufacturing differences, thus producing different waste streams. Although the ratios differ, it appears that the TCDD contamination, at least to some extent, was a product of the hexachlorophene manufacturing.

Acknowledgments

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